

METALLIZATION OF ALUMINUM NITRIDE CERAMIC (REVIEW)

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An information-analytical study of metallization technology for aluminum nitride ceramic is performed. Development work on thin- and thick-film technologies for metallization of AlN ceramic is being widely conducted in domestic and foreign enterprises. Various articles for electronic technology have been developed using metalized AlN articles.

Key words: aluminum nitride, ceramic, substrate, strength, thermal conductivity, metallization.

An important problem of modern technology in connection with the development of highly reliable, fast, high-power devices is removing heat, since heat degrades reliability and shortens the service life of electronic devices. Heat-conducting materials can help to solve this problem [1].

Possible heat-conducting materials for this are beryllium oxide BeO, silicon carbide SiC, aluminum nitride AlN and boron nitride BN.

However, beryllium oxide is toxic, silicon carbide is a semiconductor with poor dielectric properties and boron nitride requires complicated technological methods to manufacture articles. Aluminum nitride has the optimal set of properties and is nontoxic and articles can be manufactured from it by simple and efficient methods [2].

Aluminum nitride ceramic used in radio and electronic engineering at the last step of production of an article undergoes metallization followed by bonding soldering with metal structures.

Ceramic is metalized in order to create a current conducting layer on a part of the article's surface serving as an electrode as well as to obtain a strong, and in some cases vacuum-tight, ceramic–metal connection, i.e., to create a metal-ceramic structure. Metallization is also done to deposit thin-layer of metallic components of an electronic circuit on ceramic bases, substrates and other articles [3].

The choice of metal and technology of metallization depends on the purpose, shape and dimensions of the metal coating as well as the operating conditions. For the most part, precious metals — Ag, Au and Pt — are used to deposit electrically conduction layers. Aluminum and its alloys, refrac-

tory metals — W, Mo, Ta, Cr and iron-group alloys — are used for the electron components [4].

The thickness of metallic coatings varies from fractions to several tenths of a micron and depends on the purpose of the coating. Metallization is said to be thin-film for coating thickness to several microns and thick-film for thicker coatings [3].

In the thick-film technology, a layer of finely disperse metal on organic binder, secured by burn-in, is deposited on the surface of a ceramic. In the thin-film technology, a metal film is sputtered on a ceramic surface by condensation of atoms or ions [4].

The metal–ceramic interaction is due to chemical and physical adsorption processes, mechanical bonding and diffusion. When a ceramic is metalized a multilayer transitional zone consisting of the products of chemical interaction arises at the metal–ceramic interface [4].

To increase the mechanical bonding between the film and the substrate with thick-film metallization technology low-melting additives in the form of glass solders and other fluxes are introduced into the pastes [4].

The thin-film technology is more complicated. Plasma and arc spaying on pre-sintered ceramic in special facilities are used. Thin-film metallization requires the surface of the article to have a very high degree of purity with an adsorbed water vapor and other substances removed completely [3].

In [5] thin-film metallization was accomplished by depositing different substances from the vapor phase by rf sputtering in vacuum. For better adhesion, copper or aluminum to 5 μm thick was deposited on a 0.03–0.05 μm thick sublayer of chromium or other metals, such as nichrome, tungsten, titanium and molybdenum. A layer of gold or nickel was deposited to prevent a chemical reaction of the film.

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In the manufacture of high-power modules, the authors of [6] used aluminum nitride AlN and beryllium oxide BeO substrates to secure reliably operation for modules and high-voltage insulation as well as the lowest possible heat resistance. In the opinion of the authors, the range of application of AlN in engineering is wider than that of BeO because of the latter's toxicity. In addition, the thermal expansion coefficient of AlN ceramic is closer to that of silicon than in the case of BeO. This makes AlN substrates better from the engineering standpoint [5].

The authors of [5] propose a combined technology for obtaining on ceramic plates a thick copper layer suitable for efficient operation with currents >50 A and voltages 1 – 4 kV. The required thick layer of a conductor is attained by galvanic metallization of thin-film conductors prepared beforehand. This technology gives good metal – ceramic adhesion.

The conditions for plasma – arc sputtering of Mo and Ti films on AlN ceramic were studied in [6]. The ceramic samples are prepared beforehand by mechanical polishing and chemical removal of grease in toluene, after which they were heated in air at 600°C for 1 h to remove the toluene. Mo and Ti ingots served as the sputtered material. In the course of the arc discharge the cathode material eroded from the moving cathode spot and then the eroded material, comprising a directed flow of neutral atoms, ions and macroparticles, condensed on the AlN ceramic. The sputtering time was chosen on the basis of the required thickness of the metallized layer. The adhesion strength of the sputtered film with the ceramic, measured by the detachment method, served as the metallization quality criterion. The parameters for the metallization of AlN ceramic by plasma-arc spraying of Mo and Ti and the composition of the films obtained are presented in Table 1.

X-ray microprobe analysis and petrographic studies enabled the authors of [7] to propose that Ti penetrates into the ceramic and interacts chemically on the interface boundary. A thin transitional layer up to 1 μm thick, formed when Ti interacts with AlN, was observed between the ceramic and the Ti film.

This result obtained in [6] agrees with a thermodynamic calculation of the isobaric-isothermal potential of the reaction occurring according to the equation presented.

Examination of polished sections in a scanning electron microscope showed average grain size 2 – 10 μm in the ceramic and the presence of a transitional layer about 1 μm thick on the phase boundary. The thickness of the sputtered films was 1 – 2 μm for Ti and 0.5 – 0.9 μm for Mo.

As a result of their work the authors of [6] performed metallization of AlN ceramic by vacuum plasma-arc sputtering of Mo and Ti achieving adhesion strength > 50 MPa with the metal film.

The results of an investigation of the technical parameters of microwave transistors in a case with a metallized base made of aluminum nitride are presented in [7]. The metallization of ceramic was obtained by successively sputter-

TABLE 1. Conditions for Metallization of AlN Ceramic Samples and Film Properties

Metal	Spraying regime		Film properties	
	Preliminary treatment of substrate	Sputtering time, h	Thickness, μm	Adhesion strength, MPa
Mo	Heat-treatment	2.66	9.5	> 50
Mo	Heat-treatment and ionic cleaning	1.5	7.4	> 50
Ti	Heat-treatment	0.8	20.0	> 50

ing Ti and Pt layers with thickness 0.2 ± 0.02 μm and 0.15 ± 0.02 μm , respectively. Next, galvanic deposition of Ni and Au layers 1 and 4 μm thick, respectively, was performed on the Pt layer.

A comparative analysis of electric and thermal parameters of transistors using AlN and BeO ceramics showed that the output power and the power gain are practically the same for both types of transistors. The power dissipation at the same crystal temperatures for transistors made with BeO ceramic was 35 – 40% higher than for AlN ceramic [7].

The American Technical Ceramics Company [9] manufactures special hybrid passive integrated circuits (HPIC) made by thin-film technology. The company is proposing a wide spectrum of solutions and services for developers of articles for electrical engineering at the R&D stage and for us in serial production.

Special technical equipment makes it possible to obtain stable structures of high quality and high reliability. Owing to the company's technological possibilities different methods of metallization of substrates are possible.

The manufacture of different hybrid circuits requires modules with substrates with a complex configuration. Primary metallization of substrate surfaces is done, as a rule, by vacuum (magnetron) sputtering followed by galvanic formation of conducting structures. In a number of cases the conducting structures are formed on the basis of completely vacuum sputtered metals followed by etching.

HPIC include ohmic (conductors, resistors) and reactive (inductances, strip filters, matchers) elements, combined attenuators, resonators, metalized transitional openings and so forth. The range of application of special HPIC is not limited by high-frequency electronic articles. HPIC include special high-precision thin-film resistive assemblies and ceramic roller-carriers for special integrated circuits.

Thick-film technology [5] consists of depositing conducting pastes on a ceramic by serigraphic deposition (serigraphy) followed by burn-in at temperatures 650 – 1050°C. The paste is an alloy or mixture of two or more powders of metal and glassy material, creating during burn-in the required mechanical bond between the conducting parts of a metal.

Conducting pastes are often made using precious metals, since the latter are chemically inert, are distinguished by

TABLE 2. Properties of Conducting Pastes

Indicator	Paste composition					
	Ag	Pt/Au	Pd/Au	Pt/Pd/Au	Au	Pd/Ag
Specific surface resistance, Ω	0.005	0.05 – 0.12	0.05 – 0.1	0.08 – 0.1	0.003 – 0.1	0.04
Burn-in temperature, $^{\circ}\text{C}$	500 – 850	875 – 1000	900 – 975	760 – 1000	850 – 1000	690 – 760

good electric conductivity, can be soldered and welded, are compatible with substrate material, resist aging and can migrate in electric fields and surrounding media; in addition, their parameters remain stable for long times. Copper-based pastes are also used commercially. After burn-in films usually contain about 15 wt.% glassy binder — a mixture of cadmium borate or cadmium-sodium borate with bismuth oxide. A very mobile bismuth oxide in the burn-in paste creates strong adhesion, while cadmium borate improves the soldering process. The properties of the conducting compositions are presented in Table 2.

The thick-film technology makes it possible to obtain with one burn-in a conducting layer ranging in thickness from 5 to 50 μm . Successive burn-in of several layers (for example, copper-based pastes) can be used to obtain layers up to 150 μm thick.

The limitations in using the thick-film technology for high-power electronics are:

- low electric conductivity and high specific resistance of thick-film conductor compared with pure metals;
- porosity of the conducting layer and low resistance of the layer to temperatures, chemical substances and moisture;
- nonuniformity of the electric and physical properties of a conductor.

A composition of metallization paste, including a mixture of AlN and metal, chosen from a group consisting of W, Mo and their mixtures is proposed in US Patent No. 5200249 for metallization of aluminum nitride ceramic [8]. Metallization paste is used to form hermetic passage openings in an electronic assembly based on AlN ceramic. Metallization is especially useful for creating electrically conducting trough openings in bases made of AlN ceramic. Metallization paste contains a binder, dispersing agent and solvent. The role of aluminum nitride in paste is to decrease the CLTE differences between the metal and ceramic. If this difference is too large, then stresses which can lead to the formation of cracks and loss of seal appear on cooling.

The maximum amount of AlN in paste depends on the required electric conductivity. As the amount of AlN decreases, the cross-sectional area of the continuous phase of the metal and the electric conductivity decrease. The optimal content in paste is (vol.%): 5 – 75 AlN, 20 – 70 W and about 5 – 25 Mo. It is preferable to use ethyl cellulose and methylmethacrylate as the binder and terpineol as the solvent [8].

An AlN-ceramic metallization process had to be developed to assemble the body using silver-based high-temperature solder. Theoretical and experimental studies showed that

AlN-ceramic metallization is possible using pastes based on refractory metals. In the case of metallization by high-temperature burn-in of paste, because AlN-ceramic oxides aluminum oxide forming, it is very important to adhere to the temperature regimes and the requirements for the composition of the medium. Preliminary oxidation of a very thin layer of AlN-ceramic increases the adhesion of the paste to the substrate [9].

In the case of vacuum deposition of metals metallization which interacts chemically with the substrate material is preferable. In order for a chemical reaction to occur between the sputtered metal and the dielectric material, it must be possible for the reaction to occur from the stand point of thermodynamics. It has been shown that good adhesion of the metallization layer to the AlN-ceramic can be obtained by vacuum deposition of titanium as the first layer [9]. Tests for resistance to mechanical, thermal and technological actions confirmed the operational reliability of the experimental samples of the cases with AlN-ceramic heat sinks.

The authors of [10] used the sol-gel method to synthesize the glass binder for metallization of AlN substrates. The effect of the main parameters of the process, including the pH and the amount of water, was discussed. The process of sintering of a composite Ag/glass film with different glass content was studied. It was shown that glass powder with low melting temperature and chemically compatible with an AlN substrate can be obtained by the sol-gel method with the following composition (wt.%): 40 CaO, 15 B₂O₃, 35 SiO₂ and 10 BaO. During sintering the glass powder melts and has a large effect on the microstructure and surface resistance of a thin film. The optimal glass content is 10%.

The characteristics of metallization together with a heated AlN/W substrate sintered at 1650 $^{\circ}\text{C}$ were studied in [11]. The strength of the adhesion between W and the AlN ceramic could be improved by several methods, including the introduction of different mixtures of oxides or metallic particles into thick W films. In studying a mixture of the system MgO–Al₂O₃–SiO₂ the formation of glass resulted in an increase of the adhesion strength, while with the introduction of metallic particles the electric resistance of the material decreased.

Studies concerning the development of a system of glassy frits for light metallization of aluminum oxide are presented in [12]. A technology was developed to obtain glass frit for metallization containing the intermetallic compound Ti₂Cu₃ with AgCu addition with particle size <2 μm , which is most suitable for printed circuit application. The organic

media in which frit is suspended are inks containing tert-butanol, α -terpineol and polyacrylic acid. The rheological, surface and other properties of the system, its adhesion to the substrate and thermal decomposition at 850°C on heating in an inert atmosphere were studied.

The authors of [13] worked on the preparation of an AlN-ceramic surface for metallization. The effect of the temperature on the microstructure of the reaction surface in liquid media was studied. In the opinion of the authors, at the present time the water stage of cleaning of the surface of AlN substrates prior to metallization is inefficient and unreliable. This limits the use of AlN ceramic as a substitute for toxic BeO. The authors used tap and deionized water, solutions of HCl, H₂SO₄, NaOH and different concentrations, temperatures (5, 50 and 90°C) and immersion times (to 28 days) of AlN ceramic samples. The following basic changes in the microstructure were observed: average roughness of the surface, grains and formation of the synthesis reaction products. The kinetics of the change of surface roughness was very complex and depended on the reaction products, the effect of temperature on the reaction mechanism, the solvent and the pH of a specific solvent.

In summary, the data presented show that studies and development work on metallized AlN ceramic using thin- and thick-film technology are being widely pursued worldwide, and the properties of the ceramic are being studied and different articles for use in electronics are being created [14, 15]: LIC cases, transistors, heat-loaded polycrystal modules, light-emitting and microwave devices, multilayer accessory boards and other articles.

REFERENCES

1. *Technology Information: GE Advanced Ceramics*, Pub. No. 81501 09/03 (2009).
2. T. Ya. Kosolapova, *Nonmetallic Refractory Compounds* [in Russian], Metallurgiya, Moscow (1985).
3. V. L. Balkevich, *Technical Ceramics* [in Russian], Stroiizdat, Moscow (1984).
4. I. Ya. Guzman (ed.), *Chemical Technology of Ceramics* [in Russian], OOO RIF Stroimaterialy, Moscow (2003).
5. L. Islamgazina, et al., "Criteria for choosing substrates for high-power modules," *Komponenty Tekhnologii*, No. 3, 1 – 6 (2004).
6. M. V. Kuznetsov, et al., "Microstructure of metallization coatings on nitride ceramic," *Khimiya Tekhnol. Tekh. Silikatov: Tr. MKhTI*, No. 116, 21 – 23 (1980).
7. V. V. Asessorov, N. P. Butyrin, G. A. Vikin and V. A. Kozhevnikov, *Criteria for the Applicability of Ceramic Based on Aluminum Nitride in the Manufacture of Microwave Transistors* [in Russian], GP NII elektronnoi tekhniki, Voronezh (1998), p. 2.
8. Dolher, et al., *Via Metallization for AlN Ceramic Electronic Package*, US Patent No. 5200249, Issue April 6 (1993).
9. V. Sidorov, "Case for microwave transistors based on poly-diamond and aluminum-nitride ceramic," *Élektronika*, No. 4, 77 – 79 (2007).
10. Wang Lili, Wang Yu, and Yang De-An, "Glass binder in thick film metallization paste for AlN," *Key Eng. Mater.*, No. 434 – 435, 366 – 368 (2010).
11. Tongxiang Liang, Xiaoming Fu, Xueliang Qiu, et al. "Metallization development for AlN/W cofired substrate at low temperature," *J. Mater. Sci.*, **37**(10), 2163 – 2166 (2002).
12. A. Adlaßnig, J. C. Schuster, R. Reicher and W. Smetana, "Development of glass frit free metallization systems for AlN," *J. Mater. Sci.*, **33**(20), 4887 – 4892 (1998).
13. C. Deitch, et al., "Surface preparation of aluminum nitride for metallization: effect of temperature on surface reactivity," *Mater. Manufact. Processes*, **20**(5), 863 – 886 (2005).
14. M. V. Lebedev, M. A. Pavlova and Yu. N. Mushkarenko, "Particulars of manufacture of metal-ceramic units with high-temperature dielectric materials," *Élektronnaya Tekhnika, Ser. 1, SVCh-Tekhnika*, Issue 1(494), 8 – 13 (2008).
15. V. S. Seregin, L. V. Pilavova, et al., *Integrated Circuit Package, RF Patent No. 2386190, C1, H01L23/10* [in Russian], published April 10, 2010.